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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

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Triazinylaminostilbene derivatives as fluorescent whitening agents

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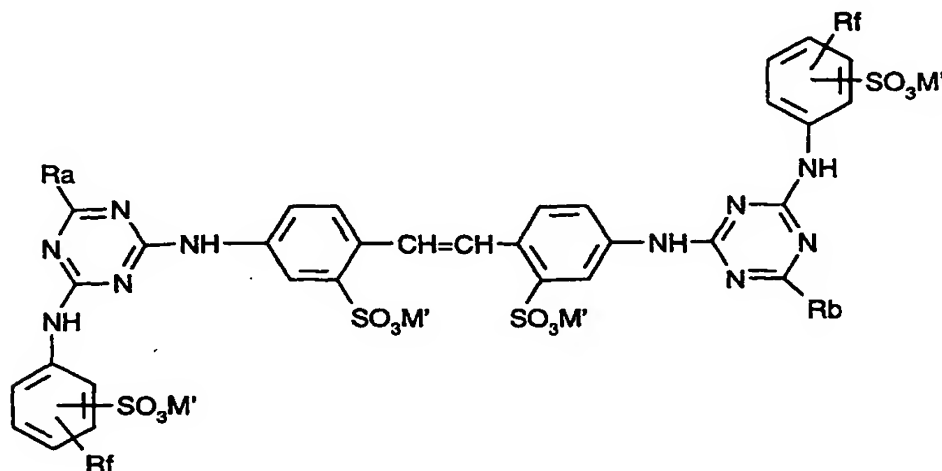
See for original title of the application
page 1 of the description

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Triazinylaminostilbene Derivatives

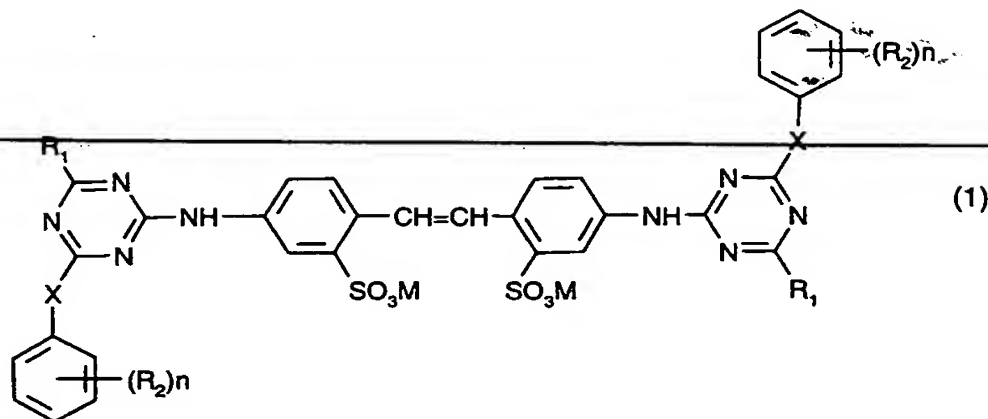
The present invention relates to new 4,4'-diaminostilbene-2,2'-disulfonic acid compounds which are useful as fluorescent whitening agents or for removing stain in photographic materials.

In WO 96/00221, there are described optical brightening agents for textiles, paper etc. The disclosed compounds have the formula:



in which R_a and R_b are the same or different and each has the formula $-NR_cR_d$ in which R_c is hydrogen; C_1 - C_6 alkyl which is optionally substituted by at least one of mercapto, C_1 - C_6 thioalkyl, OH and SO_3M' in which M' is hydrogen, a colourless cation or an amine-derived cation; or $-R_e(CO_2M')_x$ in which R_e is an aliphatic moiety having 1-6 carbon atoms, those valencies not bonded with groups CO_2M' being bonded with at least one of hydrogen, mercapto, C_1 - C_6 thioalkyl, OH and SO_3M' in which M' has its previous significance and x is an integer from 1 to 4, provided that, when R_c is C_1 - C_6 alkyl which is optionally substituted by at least one of mercapto, C_1 - C_6 thioalkyl, OH and SO_3M' , R_c is substituted with at least both of OH and SO_3M' ; R_d is R_c , hydrogen or C_3 - C_6 alkyl, provided that R_c and R_d cannot both be hydrogen and that, when one of R_c and R_d is hydrogen, the other cannot be $-(NHCH_2CO_2H)$; or R_c and R_d , together with the nitrogen atom, form a ring having from 5-6 members only, one of which is heterocyclic, which ring is singly substituted with $-COOM'$ or $-SO_3M'$; and each R_i , independently, is hydrogen, methyl, C_1 - C_6 alkoxy or halogen.

Furthermore, WO 98/42685 describes similar compounds having the formula:

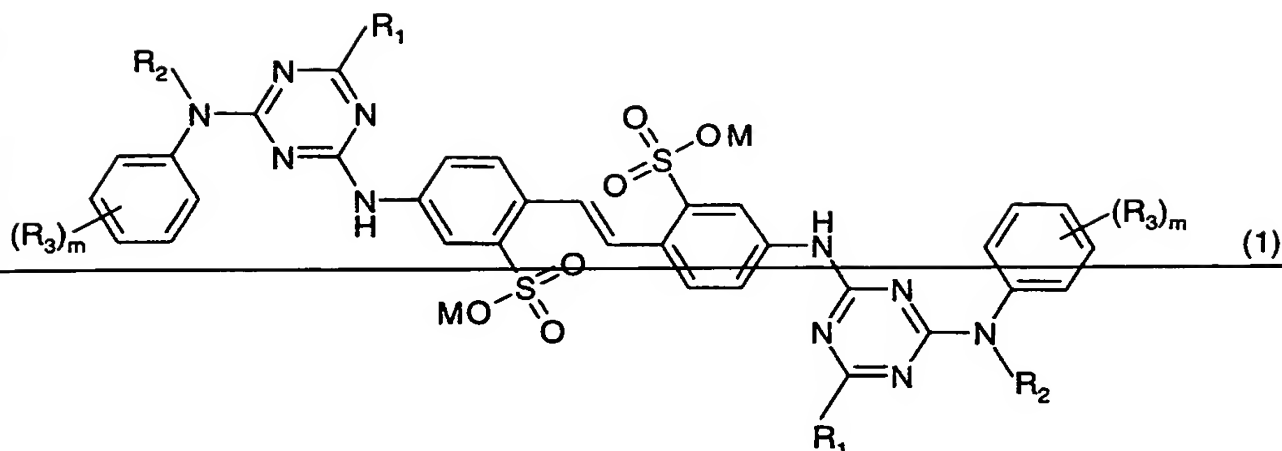


in which X is O or, preferably, NH; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; each R_1 , independently, is an amino acid residue from which a hydrogen atom on the amino group has been removed; n is 1 or 2; and each R_2 , independently, is hydrogen, C_1 - C_3 alkyl, halogen, cyano, $COOR$ in which R is hydrogen or C_1 - C_3 alkyl, $CONH-R$ in which R has its previous significance, SO_2NH-R in which R has its previous significance, $NH-COR$ in which R has its previous significance, SO_3M in which M has its previous significance or, when n is 1, R_2 can also be $CO-R_3$ in which R_3 is C_1 - C_3 alkyl or phenyl, certain compounds being excluded, and their use as fluorescent whitening agents.

A new class of 4,4'-diaminostilbene-2,2'-disulfonic acid compounds has now been found most of which are useful as fluorescent whitening agents and which have superior properties to, and are more readily prepared than the compounds disclosed in WO 96/00221 and in WO 98/42685. Furthermore, the new compounds are useful for removing stain in photographic materials.

Accordingly, the present invention provides new compounds having the formula:

- 3 -



wherein each

R_1 represents, independently, an amino acid residue from which a hydrogen atom on the amino group has been removed; each

R_2 represents, independently, a linear C_1 - C_4 -alkylene residue which is unsubstituted or substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC $_1$ - C_4 -alkyl, SO_3M , phenoxy which is unsubstituted or substituted by halogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy, - CO_2M or - CO_2C_1 - C_4 -alkyl, NH_2 or mono- or disubstituted amino, or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M , SO_2NHC_1 - C_4 -alkyl, - SO_2NH_2 , - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, - $NHCOC_1$ - C_4 -alkyl or mono- or disubstituted amino groups; each

R_3 represents, independently, hydrogen, C_1 - C_4 -alkyl, halogen, cyano, SO_3M , - SO_2NH_2 , SO_2NHC_1 - C_4 -alkyl, - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, or - $NHCOC_1$ - C_4 -alkyl;

M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and m is an integer of 1 to 3.

Within the scope of the compounds of formula (1) both of the R_1 groups, the R_2 groups and the R_3 groups are preferably identical.

Further preferred compounds of formula (1) are those in which each of the amino acid residues R_1 is the same and each has the formula $-NH-CH(CO_2H)-R_3$ in which R_3 is hydrogen or a group having the formula $-CHR_4R_5$ in which R_4 and R_5 , independently, are hydrogen or C_1 - C_4 -alkyl optionally substituted by one or two substituents selected from

hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β -indolyl, β -imidazolyl and $\text{NH}=\text{C}(\text{NH}_2)\text{NH}-$.

Particularly useful compounds of formula (1) are those in which the amino acid from which the amino acid residues R_1 are derived is glycine, alanine, sarcosine, serine, cysteine, ~~phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (~~ β -indolylalanine), histidine ((β -imidazolylalanine), α -aminobutyric acid, methionine, valine (α -aminoisovaleric acid), norvaline, leucine (α -aminoisocaproic acid), isoleucine (α -amino- β -methylvaleric acid), norleucine (α -amino-n-caproic acid), arginine, ornithine (α,δ -diaminovaleric acid), lysine (α,ϵ -diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α -aminoglutaric acid), threonine, hydroxyglutamic acid or taurine, or a mixture or an optical isomer thereof.

Especially preferred compounds are those in which the amino acid from which the amino acid residues R_1 are derived is sarcosine, taurine, glutaric acid or aspartic acid, aspartic acid or iminodiacetic acid being the most desirable.

With regard to the residue R_2 , this is preferably a methylene, ethylene or propylene residue which is substituted by hydroxy, $\text{C}_1\text{-C}_4$ -alkyl, $\text{C}_1\text{-C}_4$ -alkoxy, $\text{C}_1\text{-C}_4$ -hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC $_1\text{-C}_4$ -alkyl, -CO $_2$ M, -CO $_2$ C $_1\text{-C}_4$ -alkyl, SO $_3$ M or di-C $_1\text{-C}_4$ -alkylamino.

Compounds of particular interest are those in which R_2 is hydroxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof, hydroxyethyl or a sodium acetate residue being most preferred.

Further interesting compounds are those in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO $_3$ M, SO $_2$ NHC $_1\text{-C}_4$ -alkyl, SO $_2$ NH $_2$, CO $_2$ M, CO $_2$ C $_1\text{-C}_4$ -alkyl, -CONH $_2$, -CONHC $_1\text{-C}_4$ -alkyl, -NHCOCC $_1\text{-C}_4$ -alkyl or mono- or disubstituted amino groups.

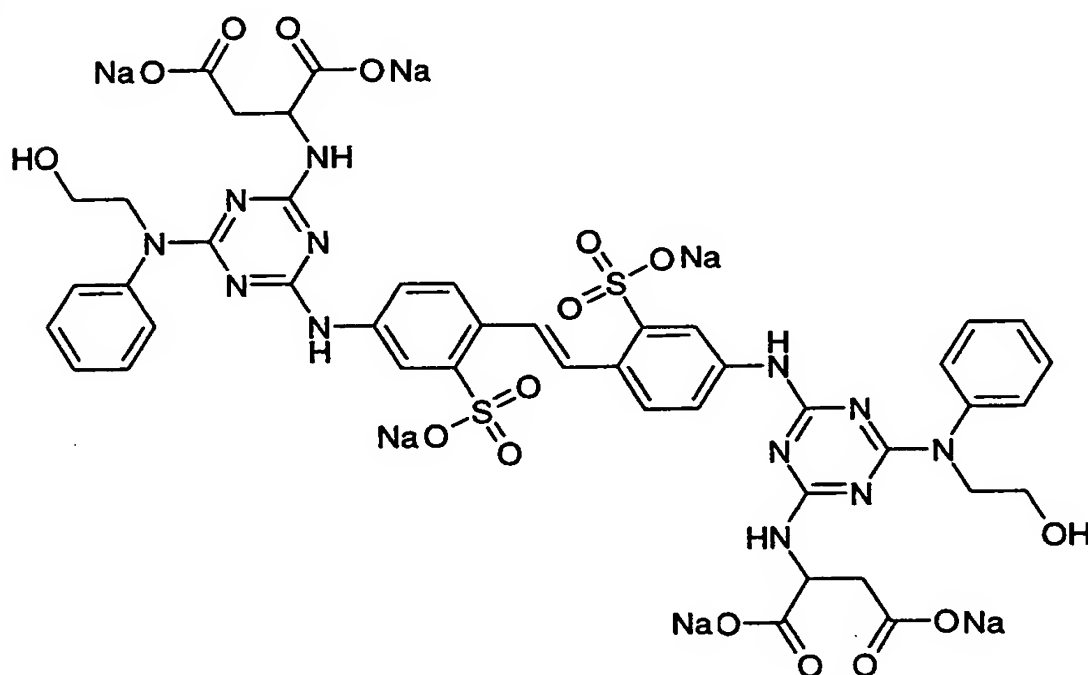
Of especial interest are compounds in which each R_2 is phenyl which is unsubstituted or substituted by one SO $_3$ M, -SO $_2$ NH $_2$ or -NHCOCC $_1\text{-C}_4$ -alkyl group, however, the phenyl group is preferably unsubstituted.

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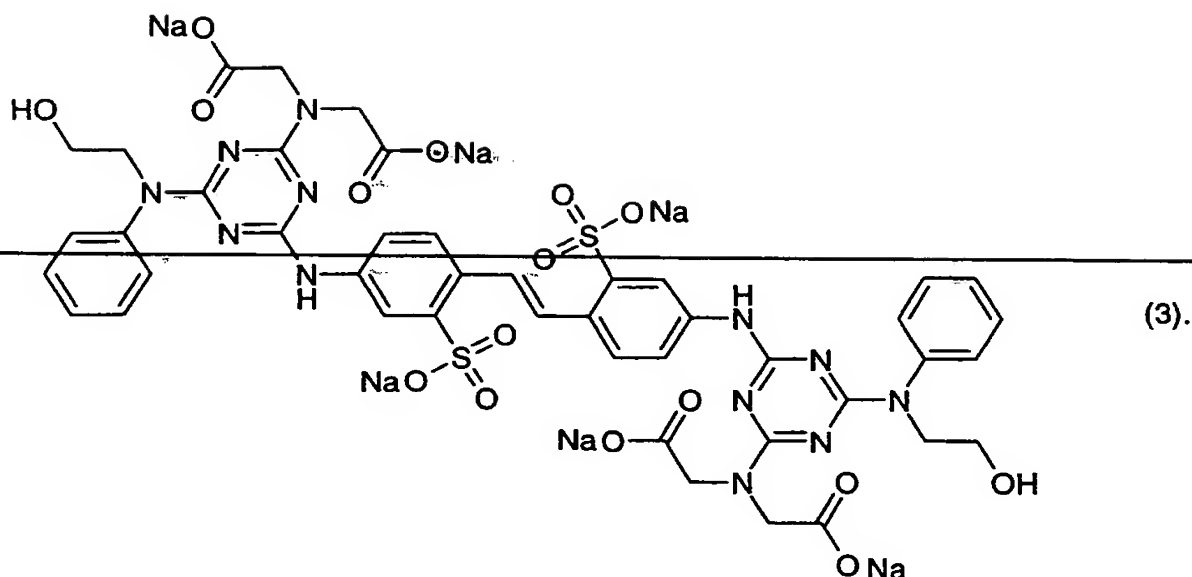
Further preferred compounds of formula (1) are those in which each R_3 residue represents hydrogen, C_1 - C_4 -alkyl, halogen, cyano, SO_3M , $-SO_2NH_2$, SO_2NHC_1 - C_4 -alkyl, $-CO_2M$, $-CO_2C_1$ - C_4 -alkyl, $-CONH_2$, $-CONHC_1$ - C_4 -alkyl, or $-NHCOC_1$ - C_4 -alkyl, those in which R_3 represents hydrogen being most preferred.

In the formulae of the above compounds, M is preferably hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- C_1 - C_4 alkylammonium, mono-, di- or tri- C_1 - C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1 - C_4 -alkyl and C_1 - C_4 -hydroxyalkyl groups, especially hydrogen or Na and m is preferably 1.

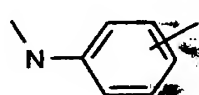
Compounds of most particular interest are those of the formula:



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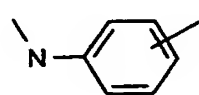


The compounds of formula (1) may be produced by reacting under known reaction conditions cyanuric chloride successively in any desired sequence with each of 4,4'-diamino-2,2'-stilbene disulfonic acid, an amino compound capable of introducing a group



in which R_3 and m have their previous significance, and a compound capable of introducing a group R_1 , in which R_1 has its previous significance.

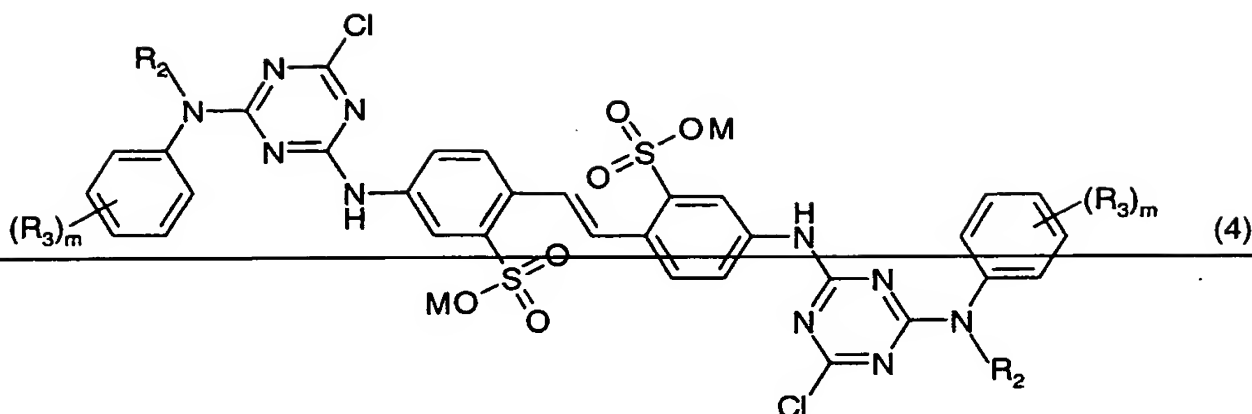
Preferably, 2 moles of cyanuric chloride are initially reacted with 1 mole of 4,4'-diamino-2,2'-stilbene disulfonic acid, then with an amino compound capable of introducing a group



in which R_3 and m have their previous significance, and, finally, with a compound capable of introducing a group R_1 , in which R_1 has its previous significance.

Consequently, a further aspect of the invention is a compound of formula:

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in which R_2 , R_3 , M and m are as previously defined.

Within the scope of the compounds of formula (4) both of the two R_2 groups and the two R_3 groups are preferably identical.

With regard to the residue R_2 , this is preferably a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC $_1$ - C_4 -alkyl, -CO $_2$ M, -CO $_2$ C $_1$ - C_4 -alkyl, SO $_3$ M or di- C_1 - C_4 -alkylamino.

Compounds of particular interest are those in which R_2 is hydroxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof, hydroxyethyl or a sodium acetate residue being most preferred.

Further interesting compounds are those in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO $_3$ M, SO $_2$ NHC $_1$ - C_4 -alkyl, -SO $_2$ NH $_2$, -CO $_2$ M, -CO $_2$ C $_1$ - C_4 -alkyl, -CONH $_2$, -CONHC $_1$ - C_4 -alkyl, -NHCOC $_1$ - C_4 -alkyl or mono- or disubstituted amino groups

Of especial interest are compounds in which each R_2 is phenyl which is unsubstituted or substituted by one SO $_3$ M, -SO $_2$ NH $_2$ or -NHCOC $_1$ - C_4 -alkyl group, however, the phenyl group is preferably unsubstituted.

Further preferred compounds of formula (4) are those in which each R_3 residue represents hydrogen, C_1 - C_4 -alkyl, halogen, cyano, SO_3M , $-SO_2NH_2$, $SO_2NHC_1-C_4$ -alkyl, $-CO_2M$, $-CO_2C_1-C_4$ -alkyl, $-CONH_2$, $-CONHC_1-C_4$ -alkyl, or $-NHCOC_1-C_4$ -alkyl, those in which R_3 represents hydrogen being most preferred.

In the formulae of the above compounds, M is preferably hydrogen, Na, K, Ca, Mg,

ammonium, mono-, di-, tri- or tetra- C_1 - C_4 alkylammonium, mono-, di- or tri- C_1 - C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1 - C_4 -alkyl and C_1 - C_4 -hydroxyalkyl groups, especially hydrogen or Na and m is preferably 1.

The starting materials are known compounds which are readily available.

A further aspect of the invention is a composition for whitening synthetic or natural organic materials or for removing stain from photographic materials, which contains water, a fluorescent whitening agent of formula (1) and, optionally, auxiliaries.

More specifically, such brightener compositions contain water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

Suitable auxiliaries include, for example, anionic or non-ionic dispersants from the class of ethylene oxide adducts with fatty alcohols, higher fatty acids or alkyl phenols or ethylenediamine ethylene oxide-propylene oxide adducts, copolymers of N-vinylpyrrolidone with 3-vinylpropionic acid, water retention aids, such as ethylene glycol, glycerol or sorbitol, or biocides.

Most of the compounds of formula (1) are excellent fluorescent whitening agents for substrates such as textiles and, in particular, for paper.

Accordingly, the present invention further provides a method for the fluorescent whitening of a substrate comprising contacting the substrate with a compound having the formula (1).

When used for the fluorescent whitening of paper, the compound of formula (1) according to the present invention may be applied to the paper substrate in the form of a paper coating composition, or directly in the size press.

In one preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and sufficient of a fluorescent whitening agent having the formula (1) according to the present invention, to ensure that the treated paper contains 0.01 to 1 % by weight, based on the white pigment, of a fluorescent whitening agent having the formula (1).

As the white pigment component of the paper coating composition used according to the method of the present invention, there are preferred inorganic pigments, e.g., aluminium or magnesium silicates, such as China clay and kaolin and, further, barium sulfate, satin white, titanium dioxide, calcium carbonate (chalk) or talcum; as well as white organic pigments.

The paper coating compositions used according to the method of the present invention may contain, as binder, inter alia, plastics dispersions based on copolymers of butadiene/styrene, acrylonitrile/butadiene/styrene, acrylic acid esters, acrylic acid esters/styrene/acrylonitrile, ethylene/vinyl chloride and ethylene/vinyl acetate; or homopolymers, such as polyvinyl chloride, polyvinylidene chloride, polyethylene and polyvinyl acetate or polyurethanes. A preferred binder consists of styrene/butyl acrylate or styrene/butadiene/ acrylic acid copolymers or styrene/butadiene rubbers. Other polymer latices are described, for example, in U.S. Patent Specifications 3,265,654, 3,657,174, 3,547,899 and 3,240,740.

The optional water-soluble protective colloid may be, e.g., soya protein, casein, carboxymethylcellulose, natural or modified starch, chitosan or a derivative thereof or, especially, polyvinyl alcohol. The preferred polyvinyl alcohol protective colloid component may have a wide range of saponification levels and molecular weights; e.g. a saponification level ranging from 40 to 100; and an average molecular weight ranging from 10,000 to 100,000.

Recipes for coating compositions for paper are described, for example, in J.P. Casey "Pulp and Paper"; Chemistry and Chemical Technology, 2nd edition, Volume III, pages 1684-1649 and in "Pulp and Paper Manufacture", 2nd and 5th edition, Volume II, page 497 (McGraw-Hill).

The paper coating compositions used according to the method of the present invention preferably contain 10 to 70% by weight of a white pigment. The binder is preferably used in an amount which is sufficient to make the dry content of polymeric compound up to 1 to 30% by weight, preferably 5 to 25% by weight, of the white pigment. The amount of fluorescent brightener preparation used according to the invention is calculated so that the fluorescent brightener is preferably present in amounts of 0.01 to 1% by weight, more preferably 0.05 to 1% by weight, and especially 0.05 to 0.6% by weight, based on the white pigment.

The paper coating composition used in the method according to the invention can be prepared by mixing the components in any desired sequence at temperature from 10 to 100°C, preferably 20 to 80°C. The components here also include the customary auxiliaries which can be added to regulate the rheological properties, such as viscosity or water retention capacity, of the coating compositions. Such auxiliaries are, for example, natural binders, such as starch, casein, protein or gelatin, cellulose ethers, such as carboxyalkylcellulose or hydroxyalkylcellulose, alginic acid, alginates, polyethylene oxide or polyethylene oxide alkyl ethers, copolymers of ethylene oxide and propylene oxide, polyvinyl alcohol, water-soluble condensation products of formaldehyde with urea or melamine, polyphosphates or polyacrylic acid salts.

The coating composition used according to the method of the present invention is preferably used to produce coated printed or writing paper, or special papers such as cardboard or photographic papers.

The coating composition used according to the method of the invention can be applied to the substrate by any conventional process, for example with an air blade, a coating blade, a roller, a doctor blade or a rod, or in the size press, after

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which the coatings are dried at paper surface temperatures in the range from 70 to 200°C, preferably 90 to 130°C, to a residual moisture content of 3-8%, for example with infra-red driers and/or hot-air driers. Comparably high degrees of whiteness are thus achieved even at low drying temperatures.

By the use of the method according to the invention, the coatings obtained are distinguished by optimum distribution of the dispersion fluorescent brightener over the entire surface and by an increase in the level of whiteness thereby achieved, by a high fastness to light and to elevated temperature (e.g. stability for 24 hours at 60-100°C.) and excellent bleed-fastness to water.

In a second preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface comprising contacting the paper in the size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20g/l of a fluorescent whitening agent having the formula (1). Preferably, the size is starch, a starch derivative or a synthetic sizing agent, especially a water-soluble copolymer.

In a third preferred aspect, the brighteners defined above are of particular importance for the treatment of textile fabrics. The treatment of textile substrates is advantageously carried out in an aqueous medium in which the particular optical brighteners are present in a finely divided form (suspensions, so-called microdispersions and in some cases solutions). Dispersing agents, stabilisers, wetting agents and further auxiliaries can optionally be added during the treatment.

The treatment is usually carried out at temperatures of from about 20° to 140°C, for example at the boiling point of the bath, or in the region thereof (about 90°C). For the finishing, according to the invention, of textile substrates it is also possible to use solutions or emulsions in organic solvents, as are used in dyeing practice in so-called solvent dyeing (pad-thermofix method and the exhaustion dyeing process in dyeing machines).

The optical brighteners which can be used according to the present invention can also be employed, for example, in the following use forms:

- (a) In mixtures with so-called "carriers", wetting agents, softeners, swelling agents, antioxidants, light stabilisers, heat stabilisers and chemical bleaching agents (chlorite bleach and bleaching bath additives).
- (b) In mixtures with crosslinking agents and finishing agents (for example starch or synthetic finishing agents) and also in combination with very diverse textile finishing processes, ~~especially synthetic resin finishes (for example crease resistant finishes such as "wash and wear", "permanent press" and "no-iron")~~, and also flame resistant finishes, soft handle finishes, anti-soiling finishes or anti-static finishes or antimicrobial finishes.
- (c) As additives to various soaps and washing agents.
- (d) In combination with other substances having an optical brightening action.

If the brightening process is combined with textile treatment or finishing methods, the combined treatment can in many cases advantageously be effected with the aid of corresponding stable formulations which contain the compounds having an optical brightening action in a concentration such that the desired brightening effect is obtained.

In certain cases, the full effect of the brightener is achieved by an after-treatment. This can be, for example, a chemical treatment (for example acid treatment), a thermal treatment (for example heat) or a combined chemical/heat treatment.

The amount of the optical brighteners to be used according to the invention, relative to the material to be optically brightened, can vary within wide limits. A distinct and durable effect can already be achieved with very small amounts and in certain cases, for example, with amounts of 0.03% by weight. However amounts of up to about 0.5% by weight can also be used. For most cases of interest in practice, amounts of between 0.05 and 0.5% by weight relative to the material to be brightened, are preferably of interest.

In a fourth aspect of the invention, the optical brighteners are also especially suitable as additives for washing baths or to industrial and household washing agents and they can be added in various ways. They are appropriately added to washing baths in the form of their solutions in water or organic solvents or also in a state of fine division as aqueous dispersions or slurries. They, or their components, are advantageously added to household or industrial washing agents at any phase of the manufacturing process of the washing agent, for example to the so-called "slurry" prior to spray-drying of the washing powder or

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during the preparation of liquid washing agent combinations. The compounds can be added both in the form of a solution or dispersion in water or other solvents and also without auxiliaries in the form of a dry brightener powder. However, they can also be sprayed, in the dissolved or pre-dispersed form, onto the finished washing agent.

~~Washing agents which can be used are the known mixtures of detergent substances, such~~
as, for example, soap in the form of chips and powders, synthetic products, soluble salts of sulphonic acid half-esters of higher fatty alcohols, arylsulphonic acids, which are substituted by higher alkyl and /or polysubstituted by alkyl, carboxylic acid esters with alcohols of medium to higher molecular weight, fatty acid acylaminoalkyl- or aminoaryl-glycerol-sulphonates, phosphoric acid esters of fatty alcohols and the like. So-called "builders" which can be used are, for example, alkali metal polyphosphates and alkali metal polymetaphosphates, alkali metal pyrophosphates, alkali metal salts of carboxyethylcellulose and other "soil redeposition inhibitors", and also alkali metal silicates, alkali metal carbonates, alkali metal borates, alkali metal perborates, nitrilotriacetic acid, ethylenediamine-tetraacetic acid and foam stabilisers, such as alkanolamides of higher fatty acids. Furthermore, the washing agents can contain, for example: antistatic agents, superfatting skin protection agents, such as lanolin, enzymes, antimicrobial agents, perfumes and dyestuffs.

The brighteners have the particular advantage that they are also effective in the presence of active chlorine donors, such as, for example, hypochlorite and can be used without substantial loss of the effects in washing baths with non-ionic washing agents, for example alkylphenol polyglycol ethers. Also in the presence of perborate or peracids and activators, for example tetraacetylglycoluril or ethylenediamine-tetraacetic acid are the new brighteners very stable both in pulverulent washing agent and in washing baths.

The brighteners according to the invention are added in amounts of 0.005 to 2% or more and preferably of 0.03 to 0.5%, relative to the weight of the liquid or pulverulent ready-to-use washing agent. When they are used to wash textiles made of cellulose fibres, polyamide fibres, cellulose fibres with a high-grade finish, wool and the like, wash liquors which contain the indicated amounts of the optical brighteners according to the invention impart a brilliant appearance in daylight.

The washing treatment is carried out, for example, as follows:

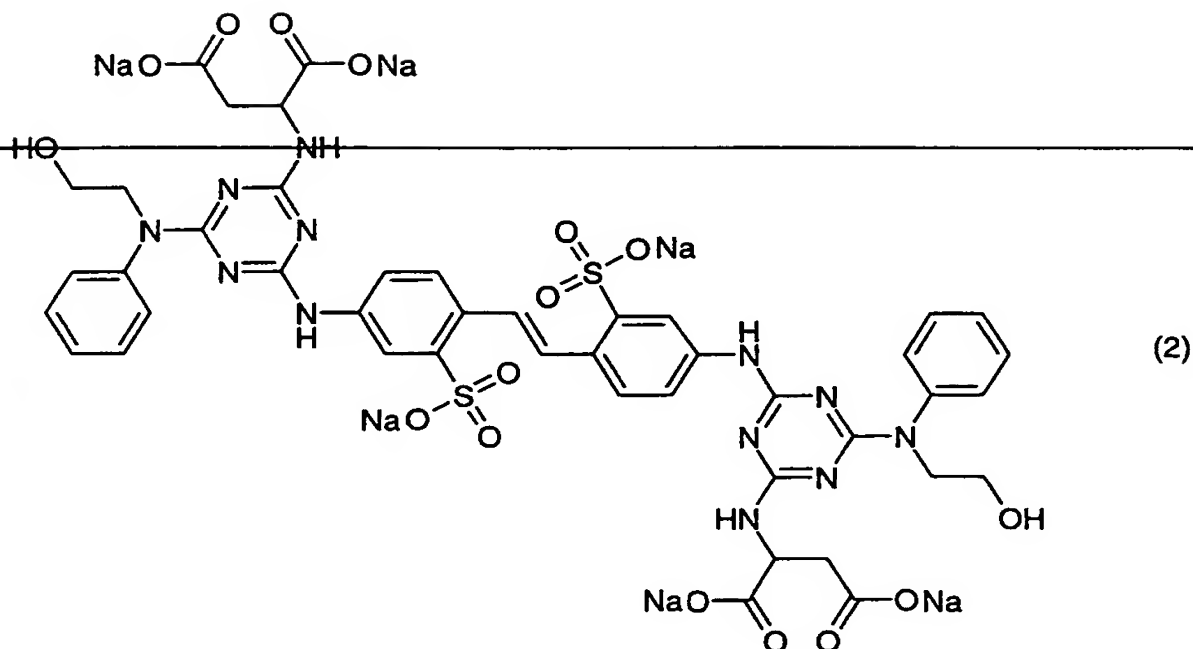
The indicated textiles are treated for 1 to 30 minutes at 5° to 100°C and preferably at 25° to 100°C in a wash bath which contains 1 to 10 g/kg of a composite washing agent containing builders and 0.05 to 1% relative to the weight of the washing agent, of the brighteners claimed. The liquor ratio can be 1:3 to 1:50. After washing, the textiles are rinsed and dried in the customary manner. The wash bath can contain, as a bleach additive, 0.2 g/l of active chlorine (for example in the form of hypochlorite) or 0.1 to 2 g/l of sodium perborate.

The brighteners according to the invention can also be applied from a rinsing bath with a "carrier". For this purpose the brightener is incorporated in a soft rinsing agent or in another rinsing agent, which contains, as the "carrier", for example, polyvinyl alcohol, starch, copolymers on an acrylic basis or formaldehyde/urea or ethylene-urea or propylene-urea derivatives, in amounts of 0.005 to 5% or more and preferably of 0.2 to 2%, relative to the rinsing agent. When used in amounts of 1 to 100 ml, and preferably of 2 to 25 ml, per litre of rinsing bath, rinsing agents of this type, which contain the brighteners according to the invention, impart brilliant brightening effects to very diverse types of treated textiles.

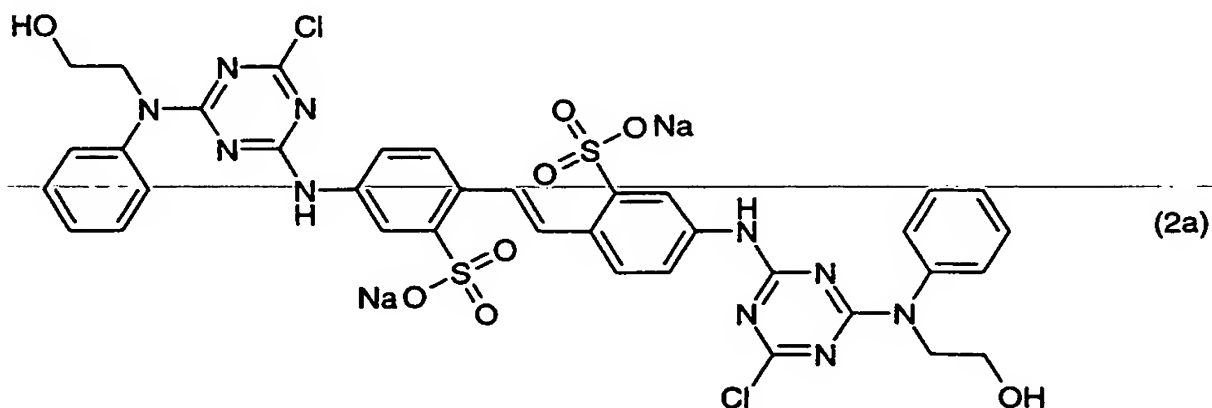
In a fifth aspect of the invention, the compounds of formula (1) are also suitable for removing stain in a photographic material which comprises a silver halide photographic light-sensitive material and, more detailedly, to a process thereof, wherein the improvement is made on the prevention of a colour stain and particularly the prevention of a colour dye stain caused in the course of processing said silver halide photographic light-sensitive material by a colour developer and a bleach-fix bath.

The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

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Example 1

18.4g. of cyanuric chloride are dissolved in 100ml. of acetone and the solution added to 100g. of ice contained in a reaction vessel. A solution of 18.4g. of 4,4'-diamino-2,2'-stilbene disulphonic acid sodium salt in 330ml. of water is then added over 10 minutes at 5°C. 50ml. of a 1 molar aqueous solution of sodium carbonate are then added over 10 minutes. 14.55g. of N-2-hydroxyethyl aniline are then added, the temperature raised to 35°C, whereby the pH is maintained between 7 and 7.5, and the mixture stirred for a further 2 hours. The precipitated product is filtered, washed with water and dried to yield 39g of a compound of formula:



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Analysis for $C_{36}H_{30}Cl_2N_{10}Na_2O_8S_2$:

calculated: C 47.32%, H 3.54%, Cl 7.76%, N 15.33%, S 7.02%;

found: C 47.1%, H 4.0%, Cl 7.7%, N 15.5%, S 6.7%.

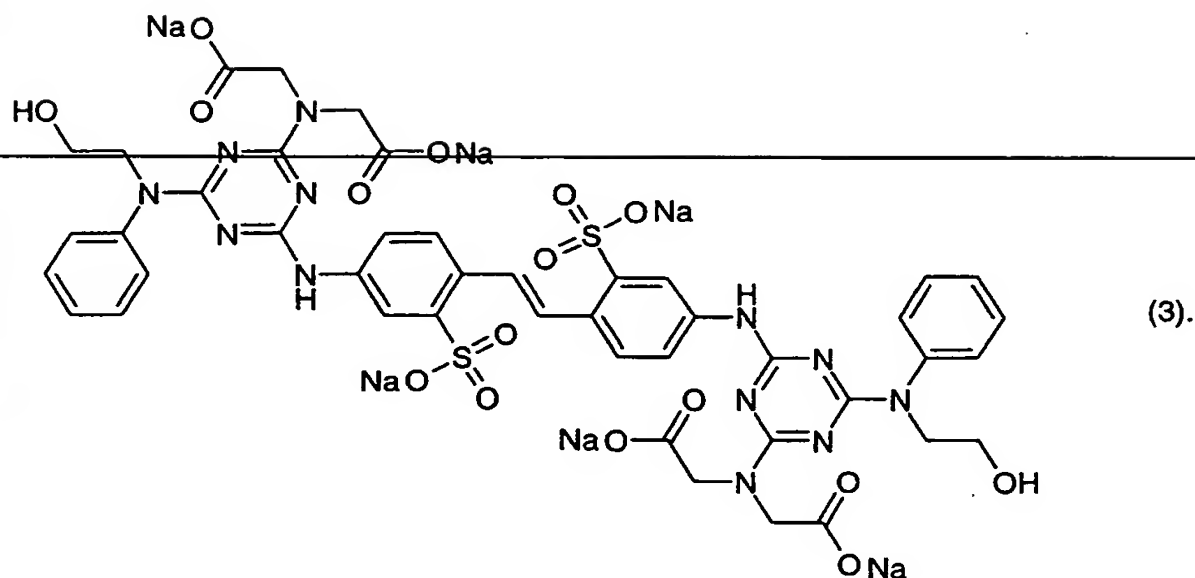
To 10g. of the compound of formula (2a) in 150ml. of water, 3.4g. of aspartic acid are added and the mixture heated to 70°C, the pH being maintained at between 8 and 8.5 by the addition of a 32% aqueous sodium hydroxide solution. After 2 hours at this temperature, the reaction is completed. The pH of the mixture is then adjusted to 3 by the addition of 37% aqueous hydrochloric acid, the temperature being maintained at 70°C. The precipitated free acid is filtered, suspended in a methanol/water mixture and the pH adjusted to 9 by the addition of a 32% aqueous sodium hydroxide solution. The precipitated product is filtered and dried to yield 8.8g of the compound of formula (2).

Analysis for $C_{44}H_{38}N_{12}Na_6O_{16}S_2 \cdot 10.5H_2O$:

calculated: C 38.23%, H 4.31%, N 12.17%, Na 9.99%, S 4.64%;

found: C 38.2%, H 4.5%, N 12.2%, Na 9.8%, S 4.6%.

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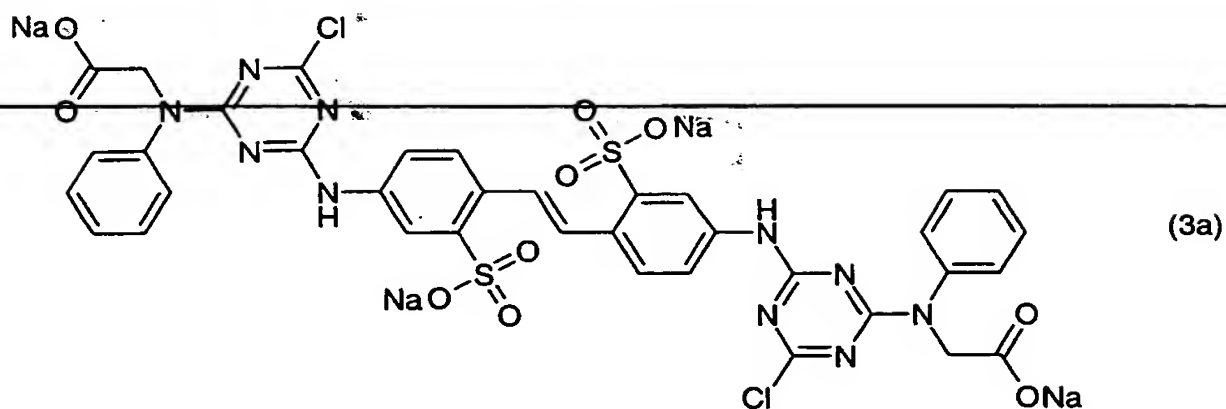
Example 2

to 40g. of ice/water, 12.5g. of cyanuric chloride are added, followed by 0.5g. of polyethylene glycol and the mixture stirred for 15 minutes. A solution of 12g. of 4,4'-diamino-2,2'-stilbene disulphonic acid sodium salt in 90ml. of water is then added over 10 minutes at 5°C. 20g. of a 17% aqueous solution of sodium carbonate in 60ml. of water are then added and the mixture stirred at 5°C until the pH falls to 5.5. The contents of the flask are then concentrated under vacuum to a weight of 193g., whereby a 20% solution of compound (2a) results which, according to HPLC, is identical to that obtained in Example (1) above.

This solution is then treated in a manner identical to that described above for the preparation of compound (2), except that the aspartic acid is replaced by the equivalent amount of iminodiacetic acid. The compound of formula (3) obtained exhibits the following elemental analysis for $C_{44}H_{38}N_{12}Na_6O_{16}S_2 \cdot 16H_2O$:

calculated: C 35.68%, H 4.75%, N 11.35%, S 4.33%;

found: C 35.52%, H 4.59%, N 11.27%, S 4.43%.

Example 3

16g. of cyanuric chloride are reacted with 16g. of 4,4'-diamino-2,2'-stilbene disulphonic acid sodium salt and then with 13.2g. of N-phenyl in a manner analogous to that described in Example 1 for the preparation of compound (2a). The resulting reaction mixture is concentrated, compound (3a) precipitated by the addition of isopropanol and isolated by filtration. The product obtained exhibits the following elemental analysis for $C_{36}H_{24}Cl_2N_{10}Na_4O_{10}S_2 \cdot 0.2NaCl$:

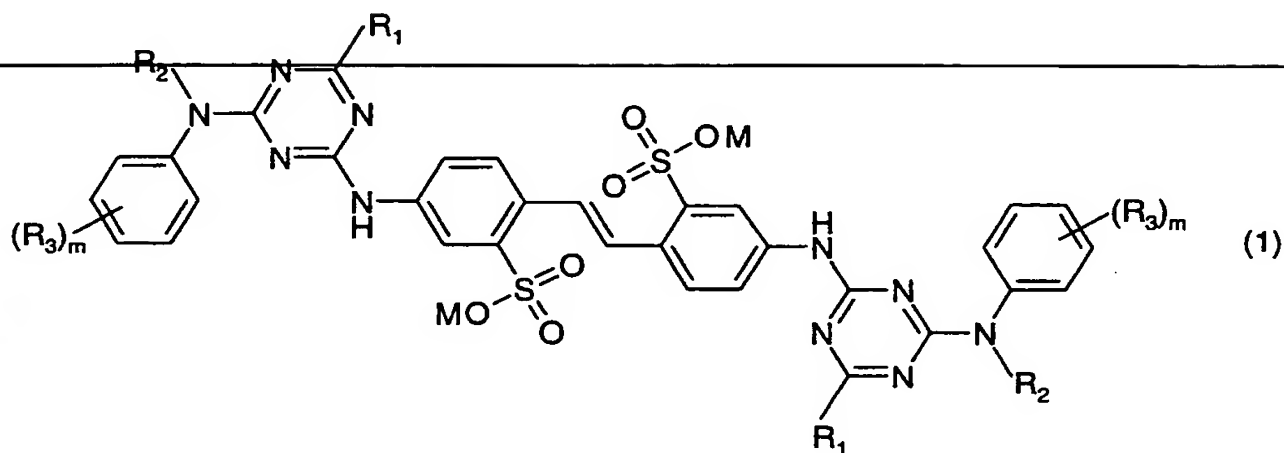
calculated: C 38.50%, H 3.45%, Cl 6.95%, N 12.50%, S 5.71%;

found: C 38.46%, H 3.60%, Cl 7.01%, N 12.59%, S 5.67%.

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Claims

1. A compound having the formula:



wherein each

R_1 represents, independently, an amino acid residue from which a hydrogen atom on the amino group has been removed; each

R_2 represents, independently, a linear C_1 - C_4 -alkylene residue which is unsubstituted or substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC $_1$ - C_4 -alkyl, SO_3M , phenoxy which is unsubstituted or substituted by halogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy, - CO_2M or - CO_2C_1 - C_4 -alkyl, NH_2 or mono- or disubstituted amino, or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M , SO_2NHC_1 - C_4 -alkyl, - SO_2NH_2 , - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, - $NHCOC_1$ - C_4 -alkyl or mono- or disubstituted amino groups; each

R_3 represents, independently, hydrogen, C_1 - C_4 -alkyl, halogen, cyano, SO_3M , - SO_2NH_2 , SO_2NHC_1 - C_4 -alkyl, - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, or - $NHCOC_1$ - C_4 -alkyl;

M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and

m is an integer of 1 to 3.

2. A compound according to claim 1 in which both of the R_1 groups, the R_2 groups and the R_3 groups are identical.

3. A compound according to claims 1 or 2 in which each of the amino acid residues R_1 is the same and each has the formula $-NH-CH(CO_2H)-R_3$ in which R_3 is hydrogen or a group having the formula $-CHR_4R_5$ in which R_4 and R_5 , independently, are hydrogen or C_1 - C_4 -alkyl optionally substituted by one or two substituents selected from hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β -indolyl, β -imidazolyl and $NH=C(NH_2)NH-$.

4. A compound according to claim 3 in which the amino acid from which the amino acid residues R_1 are derived is glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β -indolylalanine), histidine (β -imidazolylalanine), α -aminobutyric acid, methionine, valine (α -aminoisovaleric acid), norvaline, leucine (α -aminoisocaproic acid), isoleucine (α -amino- β -methylvaleric acid), norleucine (α -amino-n-caproic acid), arginine, ornithine (α , δ -diaminopivaleric acid), lysine (α , ϵ -diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α -aminoglutaric acid), threonine, hydroxyglutamic acid or taurine, or a mixture or an optical isomer thereof.

5. A compound according to claim 4 in which the amino acid from which the amino acid residues R_1 are derived is sarcosine, taurine, glutaric acid or aspartic acid.

6. A compound according to any of claims 1 to 5 in which the amino acid from which each amino acid residue R_1 is derived is aspartic acid or iminodiacetic acid.

7. A compound according to any one of claims 1 to 6 in which the group R_2 represents a linear C_1 - C_4 -alkylene residue which is unsubstituted or substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy or alkoxyalkoxy, $-OCOM$, $-OCOC_1$ - C_4 -alkyl, SO_3M , phenoxy which is unsubstituted or substituted by halogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy, $-CO_2M$ or $-CO_2C_1$ - C_4 -alkyl, NH_2 or mono- or disubstituted amino.

8. A compound according to claim 7 in which the group R_2 represents a methylene, ethylene or propylene residue which is substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy- or alkoxy-alkoxy, $-OCOM$, $-OCOC_1$ - C_4 -alkyl, $-CO_2M$, $-CO_2C_1$ - C_4 -alkyl, SO_3M or di- C_1 - C_4 -alkylamino, whereby M is as defined in claim 1.

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9. A compound according to claims 7 or 8 in which R_2 is hydroxyethyl, hydroxypropyl, ethoxyethyl, hydroxyethoxyethyl, methoxyethoxyethyl, an acetic or propionic acid residue or methyl or ethyl esters thereof, an ethyl or methyl acetate, dimethylaminoethyl or ethyl sulphonic acid or the sodium salt thereof.

~~10. A compound according to claim 9 in which R_2 is hydroxyethyl or a sodium acetate residue.~~

11. A compound according to claims 1 or 2 in which each R_2 is phenyl which is unsubstituted or substituted by 1 to 3 SO_3M , $SO_2NHC_1-C_4$ -alkyl, $-SO_2NH_2$, $-CO_2M$, $-CO_2C_1-C_4$ -alkyl, $-CONH_2$, $-CONHC_1-C_4$ -alkyl, $-NHCOC_1-C_4$ -alkyl or mono- or disubstituted amino groups, wherein M is as defined in claim 1,

12. A compound according to claims 11 in which each R_2 is phenyl which is unsubstituted or substituted by one SO_3M , $-SO_2NH_2$ or $-NHCOC_1-C_4$ -alkyl group.

13. A compound according to claims 11 or 12 in which each R_2 is phenyl.

14 A compound according to any one of the preceding claims in which R_3 represents hydrogen, C_1-C_4 -alkyl, halogen, cyano, SO_3M , $-SO_2NH_2$, $SO_2NHC_1-C_4$ -alkyl, $-CO_2M$, $-CO_2C_1-C_4$ -alkyl, $-CONH_2$, $-CONHC_1-C_4$ -alkyl, or $-NHCOC_1-C_4$ -alkyl, M being defined as in claim 1 and m is 1.

15. A compound according to claim 14 in which R_3 represents hydrogen.

16. A compound according to any of the preceding claims in which M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- C_1-C_4 alkylammonium, mono-, di- or tri- C_1-C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4 -alkyl and C_1-C_4 -hydroxyalkyl groups.

17. A compound according to claim 16 in which each M is hydrogen or Na.

18. A compound of formula 1 in which:
 R_1 is hydroxyethyl,

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R_2 is an amino acid residue derived from aspartic acid,
 R_3 is hydrogen and
 M is sodium.

19. A compound of formula 1 in which:

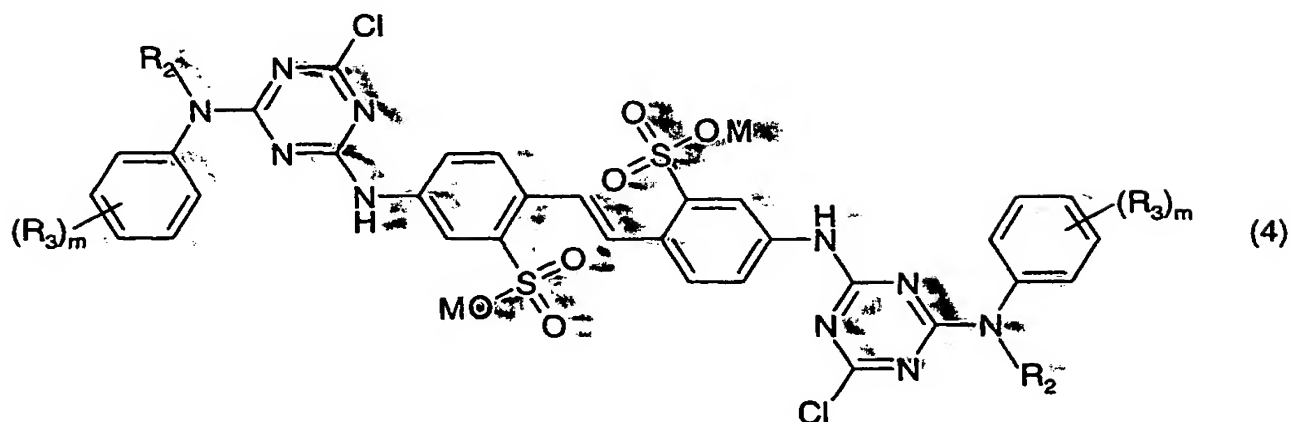
R_1 is hydroxyethyl,

R_2 is an amino acid residue derived from iminodiacetic acid,

R_3 is hydrogen and

M is sodium.

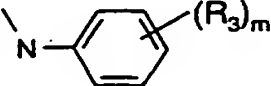
20. A compound of the formula:



in which R_2 , R_3 , M and m are as defined in claim 1.

21. Use of the compound of formula (2) of claim 20 for the preparation of a compound of the formula (1).

22. A process for the preparation of a compound of formula (1) by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diamino-2,2'-stilbene disulphonic acid, an amino compound capable of introducing a

group  in which R_3 and m have their previous significance, and a

compound capable of introducing a group R_1 , in which R_1 has its previous significance.

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23. Use of the compounds of formula (1) as optical brightening agents for synthetic or natural organic materials.

24. Use of the compounds of formula (1) according to claim 22 as optical brightening agents for paper in pulp, size-press or coating applications.

25. Use of the compounds of formula (1) according to claim 22 as optical brightening agents for textile materials, especially cotton and polyamide materials as well as mixtures of the same and other synthetic fibres.

26. Use of the compounds of formula (1) according to claim 22 as optical brightening agents in detergent compositions.

27. Use of the compound of formula (1) for removing stain in photographic materials.

28. A composition for whitening synthetic or natural organic materials or for removing stain from photographic materials, which contains water, a fluorescent whitening agent according to claim 1 and, optionally, auxiliaries.

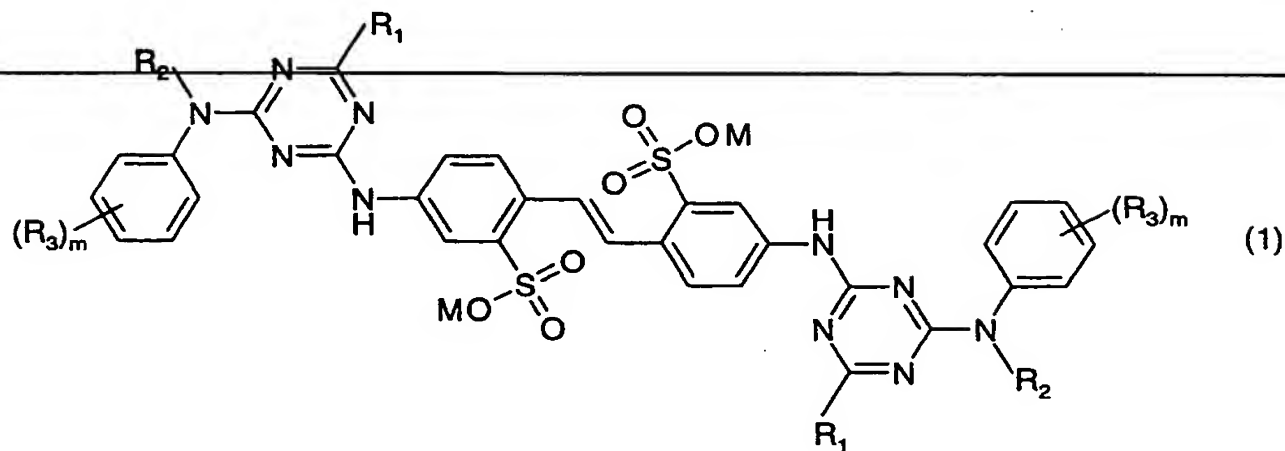
29. Brightener compositions according to claim 27 containing water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

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Abstract

The present invention relates to compounds having the formula:



wherein each

R_1 represents, independently, an amino acid residue from which a hydrogen atom on the amino group has been removed; each

R_2 represents, independently, a linear C_1 - C_4 -alkylene residue which is unsubstituted or substituted by hydroxy, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -hydroxy- or alkoxy-alkoxy, -OCOM, -OCOC $_1$ - C_4 -alkyl, SO_3M , phenoxy which is unsubstituted or substituted by halogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy, - CO_2M or - CO_2C_1 - C_4 -alkyl, NH_2 or mono- or disubstituted amino, or phenyl which is unsubstituted or substituted by 1 to 3 SO_3M , SO_2NHC_1 - C_4 -alkyl, - SO_2NH_2 , - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, - $NHCOC_1$ - C_4 -alkyl or mono- or disubstituted amino groups; each

R_3 represents, independently, hydrogen, C_1 - C_4 -alkyl, halogen, cyano, SO_3M , - SO_2NH_2 , SO_2NHC_1 - C_4 -alkyl, - CO_2M , - CO_2C_1 - C_4 -alkyl, - $CONH_2$, - $CONHC_1$ - C_4 -alkyl, or - $NHCOC_1$ - C_4 -alkyl;

M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine and

m is an integer of 1 to 3, a process for their preparation and use of the compounds as optical brightening agents for synthetic or natural organic materials or for removing stain in photographic materials.

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